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Critical Loads of Acid Deposition for Surface Water

Exploring existing models and a potential alternative for Sweden

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Abstract

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Cutting down emissions of sulphur and nitrogen compounds is the most obvious long-term solution to the acidification problem. The critical load concept has proved a very useful basis for the European negotiations about how much the emissions have to be reduced in order to protect the environment. Great reductions have been achieved and in the near future we are facing a situation where we have to decide to what extent further emission reductions are needed. To be able to make such decisions, we have to take into account the uncertainties of the critical load concept. Otherwise, incorrect decisions may result in further acidification or, on the contrary, economical investments without due cause.

The main objectives of this thesis are to validate and elucidate the model used in Sweden to determine the critical load of acidity for surface waters i.e. the steady state water chemistry model (SSWC) as well as to explore a potential alternative (PROFILE). As a way of testing the models, diatom reconstructions of pre-industrial lake chemistry are used. The acidification status of Swedish surface waters was also assessed with particular attention to uncertainties.

The SSWC model's prediction of pre-industrial pH did not correspond well with the diatom reconstructions for pH values below 6.5. The discrepancies can be related to short-term fluctuations in modern lake chemistry.

Applying the F-factor (a component of SSWC) to time series of runoff chemistry generated by the SAFE model suggests that the F-factor worked best during the acidification phase when soil processes buffer incoming acidity. However, the empirical functions for estimating F from contemporary lake chemistry are not well adapted to the recovery phase when the F-factor turns negative due to recovery processes in the soil.

Exploring the PROFILE model as an alternative to SSWC revealed that calculating critical loads for individual lakes is not feasible when using the PROFILE model due to lack of catchment specific input data. However, the use of soil parameter distributions is possible since the critical loads used in international negotiations are not for individual sites but for distributions of ecosystems in large areas. While direct consideration of soil properties instead of lake chemistry is promising, there are problems of hydrology, data acquisition and spatial integration which will have to be overcome if PROFILE is to be a viable alternative for calculating surface water critical loads.

Key words: critical loads, surface waters, lakes, acidification, steady state water chemistry, SSWC, F-factor, palaeolimnology, PROFILE, SAFE, Sweden

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Appendix

Papers I-IV

The present thesis is based on the following papers which are referred to by their Roman numerals.

I. Rapp, L., Wilander, A., Laudon, H. and Bishop, K. 2001. Acidification and Natural Acidity of Swedish Lakes. Manuscript

II. Bishop, K., Rapp, L., Köhler, S. and Korsman, T. 2001. Testing the Steady-State Water Chemistry Model Predictions of Pre-industrial Lake pH with Paleolimnological Data from Northern Sweden. Submitted

III. Rapp, L., Wilander, A. and Bishop, K. 2001. Surface Water Acidification and Critical Loads: Exploring the F-factor. Manuscript

IV. Rapp, L. and Bishop, K. 2001. Modelling Surface Water Critical Loads with PROFILE: Possibilities and Challenges. Manuscript

What this thesis is all about.....

Cutting down emissions of sulphur and nitrogen compounds is the natural and the most obvious long-term solution to the acidification problem. The critical load concept has proved to be a very useful basis for the European negotiations about how much the emissions have to be reduced in order to protect the environment. Great reductions have been achieved and in the near future we are facing a situation where we have to decide whether or not further emission reductions are needed. To be able to make such decisions, we have to take into account the uncertainties of the critical load concept. Otherwise, incorrect decisions may result in further acidification or, on the contrary, economical investments without due cause. These developments call for a review of current methods for calculating how much acid deposition nature can tolerate, *i.e.* the critical load.

This thesis focuses on critical loads for surface waters. The main objectives are to test and elucidate the method that has been used for calculating critical loads of acidity in Sweden (the SSWC model) and explore an alternative way to proceed (the PROFILE model).

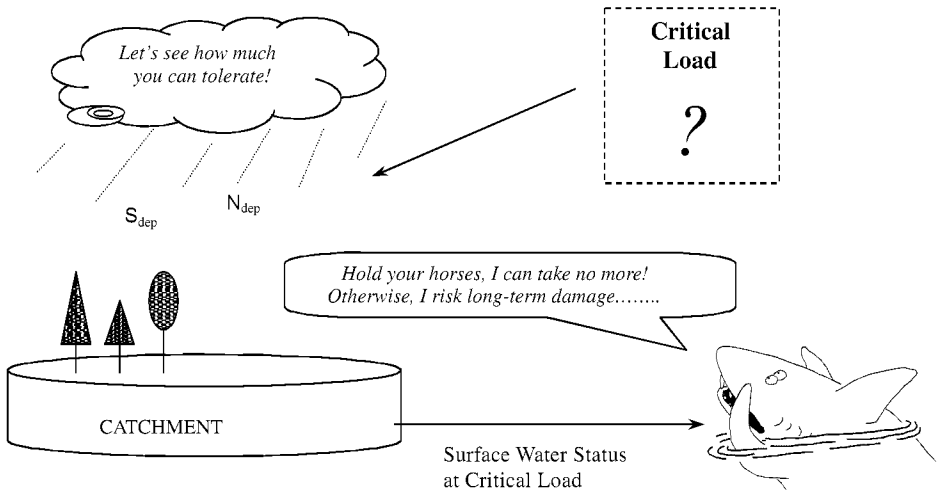

Fig. 1. This thesis deals with the models used for calculating critical loads (CL) of acid deposition for lakes. Do they work and are there better alternatives?

Introduction

How to address the acidification issue?

In the late 60s, an article about acidified precipitation was published in a Swedish newspaper where the author, Svante Odén, (Odén, 1967) argued that acid deposition was a result of human activities like burning of oil. Most important, he claimed that these activities were causing acidification that led to fish death, decreased forest productivity and other negative effects on the environment.

Even if other researchers had thought in similar ways before this time, it is often said that this article marked the beginning of decades of debate, research and controversies about acid rain (Lundgren, 1991). Major research efforts were undertaken to establish the causes and effects of acid precipitation. Despite the intense scientific focus, though, it took almost two decades to prove the connection between acid deposition and acidification to the satisfaction of several major protagonists. Many new scientific issues also arose in the process.

Once accepted as a problem, the need for acidification abatement strategies was recognised. In the short term, liming may be a solution. However, in the long run a better solution would be to cut down the emissions to acceptable levels. There are, however, a number of obstacles and considerations to be dealt with in achieving such a goal.

To begin with, cutting down emissions is not a straightforward procedure as there are no national borders for acid deposition, i.e. acidification is a global problem. Consequently, an individual country may not be responsible for its own acidification. Furthermore, abatement strategies require economical investments and technical knowledge. Here an inevitable question arises; how can a single country be convinced to pay for somebody else's problem? Finally, all European countries do not have the same possibilities, for economic reasons, to make the arrangements needed to decrease their emissions. Thus, it is clear that it takes political, economic and technical considerations to address the acidification issue.

The Geneva Convention on Long Range Transboundary Air Pollution (CLRTAP) in 1979 represents the first step towards international agreements between European countries on emission reductions organised by the United Nations Economic Commission for Europe (UN/ECE). A sulphur protocol was developed in 1985 and by 1990 the protocol was signed by 21 European countries as well as USA and Canada. The protocol stated that the signatories should reduce their sulphur emissions to at least 30% below 1980 levels by 1993. Thus, the commitments to reduce emissions were spread evenly over Europe.

How much does nature tolerate – what is the critical load?

A growing awareness of the need to optimise abatement strategies pushed forward the need to locate the most sensitive areas. A Canadian study (Eldar et al., 1983), argued that there was a sulphur load below which no harmful effects to fish stocks occurred. Canada went on to become the first country that coupled the sulphur deposition load to what nature can tolerate, i.e. the critical load of sulphur. A critical load is defined as (UNECE, 1994):

"a quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified elements of the environment do not occur, according to present knowledge"

The critical load concept thus offers a way for quantifying how much of different pollutants nature can tolerate. With respect to acidification these pollutants are sulphur and nitrogen. The critical load concept was first used as the basis for an international agreement on pollution control in the second sulphur protocol, established in Oslo (UNECE, 1994). The concept is also applied to other pollutants *e.g.* heavy metals and ozone, but the following description deals only with sulphur and nitrogen.

Calculation of critical loads

Starting up

Before we are able to calculate the critical load, some key steps have to be considered. First of all the ecosystem has to be defined, in this case a lake and its catchment. Then a biological indicator is chosen representing a sensitive component of the ecosystem. To quantify if and when harmful effects occur, the response of the indicator is coupled to a chemical criterion, which in turn relates to a critical chemical value of this criterion. For Swedish lakes, the biological indicator is fish, the chemical criterion is Acid Neutralising Capacity (ANC) and the critical chemical value is 20 $\mu eq\ L^{-1}$.

Finding the critical load of sulphur and nitrogen

The main issue of critical load models is to relate acid deposition to the chemical criteria. This takes models that simplify the biological and geochemical properties of nature, in order to make the concept feasible. One crucial feature of the models is the steady-state approach, meaning that short-term processes are not taken into account. One way of illustrating steady-state is to outline the course of events during lake acidification and the subsequent recovery (Figure 2).

I. At the beginning, in pre-industrial times, lake chemistry was at steady-state with atmospheric deposition. Finding this lake chemistry is the fundamental task of many acidification models, i.e. what were conditions before the human impact?

II. In the middle of the 19th century, industrialisation starts and the emissions of sulphur give rise to higher sulphur deposition (and later on nitrogen as well). Soil processes such as ion exchange and sulphur adsorption start neutralising the enhanced acidity of the precipitation. This is referred to as soil acidification because the storage of base cations decreases and is replaced by hydrogen ions and aluminium.

III. The soil buffering capacity is exhaustible and sooner or later the base cation storage is depleted. The ANC in runoff then decreases rapidly, which gives rise to lake acidification.

IV. As the sulphur deposition levels out, so does lake chemistry. A new steady-state appears.

V. The implementation of abatement strategies results in decreased deposition and the recovery phase starts. Lake ANC increases but recovery is delayed as the soil storage of base cations slowly is replenished. This phase is the reverse of phase II.

VI. Eventually, the recovery is completed and lake chemistry levels out at a new steady-state.

A steady-state model calculates the final state for a given set of conditions, but the time to reach that state is not considered. Mathematically, the time derivatives are zero at steady-state.

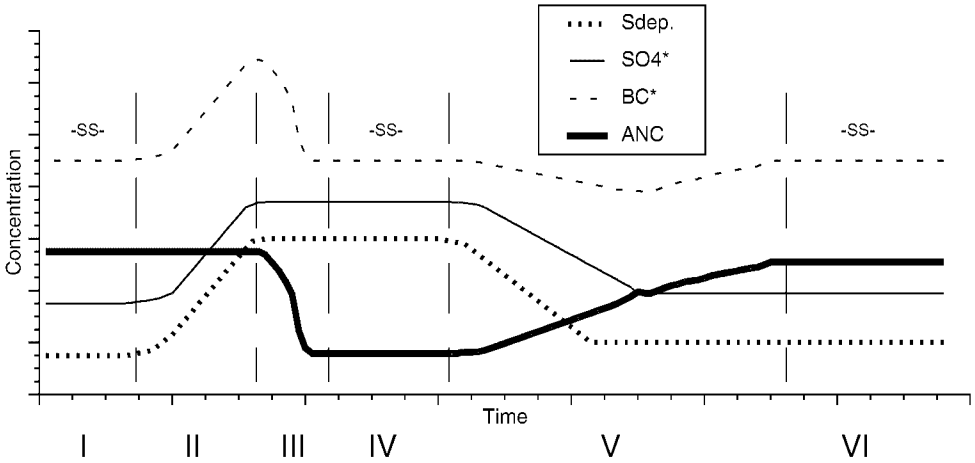

Fig. 2. A conceptual view of a lake acidification and the following recovery phase. Three steady-state (-ss-) periods are identified. The figure is extracted and modified from Rapp *et al.* (2001).

In order to calculate the critical load of acid deposition *i.e.* sulphur (S) and nitrogen (N), the most important processes involved in the production and consumption of ANC have to be considered. The SMB, Simple Mass Balance,

constitutes the starting point for many critical load models, both for lakes and forest soils. SMB is also referred to as SSMB (Steady-State Mass Balance). Through the years, these models have been discussed and modified at a number of workshops (Nilsson and Grennfelt, 1988), (Sverdrup *et al.,* 1990), (Grennfelt and Thörnelöf, 1992) and (Hornung *et al.,* 1995). The following description is a brief overview of the fundamental principles behind this approach to determining critical loads of sulphur and nitrogen. A more thorough description is found in Posch *et al.* (1995) and UBA (1996).

A simplified balance between consumption- and production of ANC of the ecosystem is the starting-point. Here charge per unit area and time (eq ha^{-1} $year^{-1}$ or similar) is used:

$$S_{dep} + N_{dep} + Cl_{dep} + BC_u + ANC_{le} = BC_w + BC_{dep} + N_u + N_i + N_{de} \qquad (1a)$$

$$ANC\ consumers \qquad = \qquad ANC\ producers \qquad (1b)$$

Deposition of sulphur, nitrogen and chloride (S_{dep}, N_{dep}, Cl_{dep}) consume ANC. Uptake of base cations (BC_u,) and leaching of ANC (ANC_{le}) are also acidifying processes in the soil. The uptake relates to the net uptake in vegetation that is removed by harvesting. Weathering (BC_w) and base cation deposition (BC_{dep}) are important long-term sources of ANC. It should also be noted that the deposition terms in equation 1 include sea salts, which do not influence ANC in a water solution.

Nitrogen is difficult to handle because it is acidifying in the same way as sulphur, but nitrogen also participates in a number of other processes in the soil and vegetation. In SMB, the total nitrogen deposition (nitrate + ammonium) consumes ANC while uptake (N_u), immobilisation (N_i) and denitrification (N_{de}) produce ANC. The underlying assumption is zero leaching of ammonium i.e. ammonium is either assimilated or nitrified to nitrate that is assimilated.

With the critical chemical value of ANC in the water leaching from the soil needed to support sensitive aquatic life, $ANC_{le.crit}$, we can define the critical load of sulphur and nitrogen deposition, CL(S+N):

$$CL(S+N) = BC_w + BC_{dep} + N_u + N_i + N_{de} - Cl_{dep} - BC_u - ANC_{le,crit} \qquad (2)$$

Equation 2 is an expression of the maximum deposition of sulphur and nitrogen, given that; i) N_{dep} is larger than the sum of N_u, N_i and N_{de} and ii) the sum of BC_w and BC_{dep} is larger than BC_u. Note that there is no unique critical load of sulphur and nitrogen. Instead there are an infinite number of combinations of S_{dep} and N_{dep}, fulfilling equation 2. However, we can define the maximum critical load of sulphur, given that the nitrogen deposition has no acidifying effect:

$$CL_{\max}(S) = BC_{dep} - Cl_{dep} + BC_w - BC_u - ANC_{le,crit} \qquad (3)$$

The nitrogen deposition causing no acidification is given by:

$$CL_{\min}(N) = N_i + N_u + N_{de} \quad (4)$$

Finally, the maximum nitrogen deposition, when the sulphur deposition is zero becomes:

$$CL_{\max}(N) = CL_{\min}(N) + CL_{\max}(S) \quad (5)$$

$CL_{max}(S)$, $CL_{min}(N)$ and $CL_{max}(N)$ form the critical load function (Figure 3), which is the key information for European work on critical loads with reference to acidification. Equations 3, 4 and 5 are the basic formulas and can be applied to both forest ecosystems and lakes. Depending on how the processes are formulated, the final expression may look different, but the principles are the same.

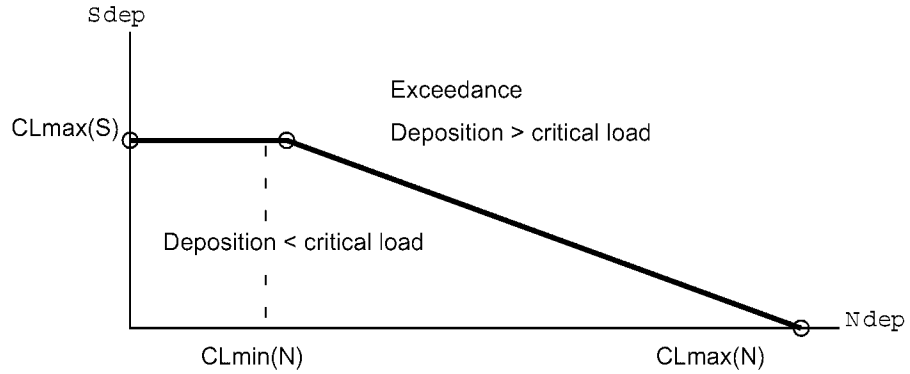

Fig. 3. The critical load function (bold line) describes all combinations of sulphur- and nitrogen deposition equal to the critical load. Deposition above the function line denotes exceedance i.e. the acid deposition is higher than the critical load.

The FAB model, First-order Acidity Balance (Kämäri et al., 1992; Henriksen et al., 1993; Downing et al., 1993; Posch et al., 1997) is the modified version of SMB to account for catchment- and lake processes. The FAB model has been applied to the Swedish National Lake Survey 1990 (Henriksen et al., 1993; Posch et al., 1997) and also the Lake Survey 1995 (Rapp et al., 2001). The latest critical load calculations, and also the ones which are currently in use in the European work within CLRTAP (Posch et al., 1999), are based on lake chemistry data from the survey in 1995 (Figure 4).

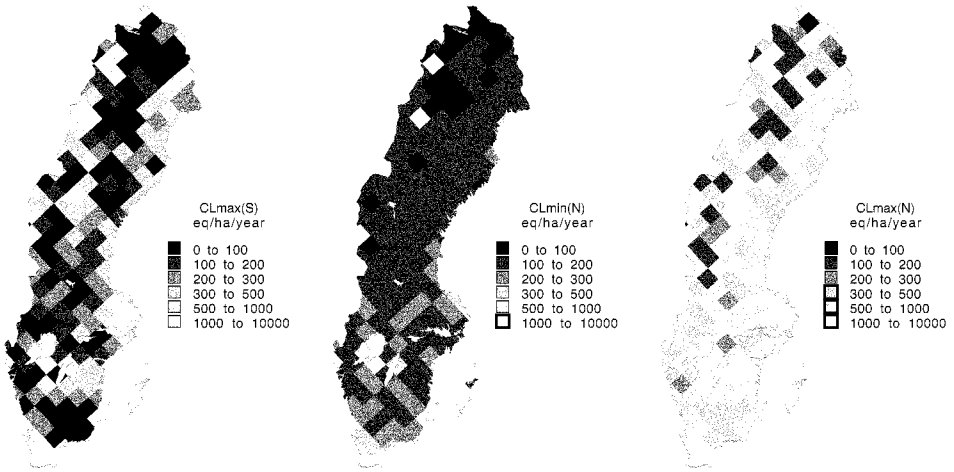

Fig. 4. Critical loads of S and N for surface waters in Sweden, eq ha^{-1} $year^{-1}$. Note that the 5^{th} percentile is shown in each grid cell. In a European perspective, large areas of the country have very low critical loads ($CL_{max}(S)$); 100 eq ha^{-1} $year^{-1}$ is equivalent to 1.6 kg S ha^{-1} $year^{-1}$. There is a distinct pattern of small nitrogen sinks ($CL_{min}(N)$) in the north which are gradually increasing to the south. It should be noted that $CL_{max}(N)$, using the FAB model, is not simply the sum of $CL_{max}(S)$ and $CL_{min}(N)$ because of the inclusion of deposition dependent processes.

Where are we today?

Data delivery to protocols

A general overview of some key steps on the way to the international negotiations on emission reductions is outlined in Figure 5.

Each country participating in the European work calculates national critical loads and decides what methods should be used and the ecosystems considered. The Coordination Center for Effects (CCE) at Rijksinstituut voor Volksgezondheid en Milieu (RIVM) in the Netherlands has a key role in this respect by offering support in preparing national critical loads.

The CCE compiles data from all countries and synthesises them into a European database. This involves preparing "ecosystem protectionisolines" (Posch *et al.*, 1995), which is a way of dealing with several CL functions (Figure 3) *i.e.* ecosystems within a grid cell of either 50/50 km or 150/150 km.

In the RAINS model (Alcamo *et al.*, 1990) CLs (protection isolines) are compared to deposition data (from emission data). Several emission scenarios are evaluated taking into account environmental objectives and the costs needed to reach the emission scenarios. Finally, these scenarios are used in the preparations of protocols to the CLRTAP.

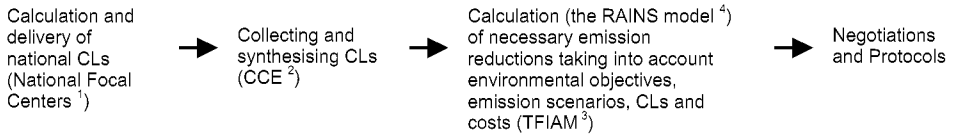

Fig. 5. A generalised view of the way from CLs to protocols.

[1] Individual countries delivering CLs

[2] Coordination Center for Effects, under the UN/ECE Working Group on Effects (WGE)

[3] Task Force on Integrated Assessment Modelling, under the UN/ECE Working Group on Strategies (WGS)

[4] Regional Air Pollution Information and Simulation

Great improvements have been made

The critical load concept has turned out to be very useful for the European negotiations on reducing transboundary air pollution. That is manifested by the 1999 Gothenburg protocol to abate acidification, eutrophication and ground-level ozone (UNECE, 1999). The full implementation of the protocol will reduce the deposition exceedance for Swedish lakes to 11% in 2010. In 1980 the situation was much worse (Figure 6).

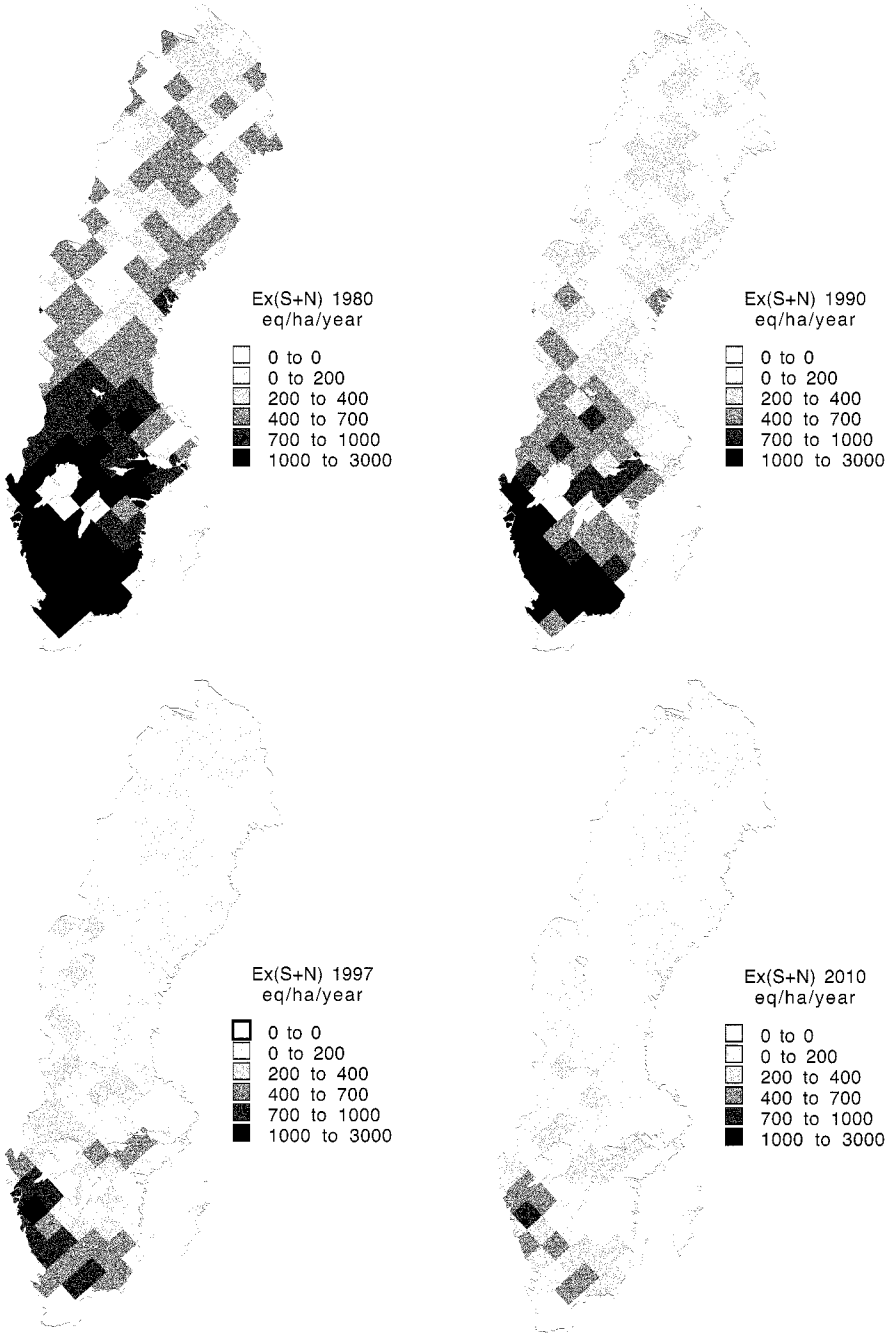

Fig. 6. Exceedance of critical loads (S+N) for surface waters in Sweden for 1980 to 2010, eq ha^{-1} $year^{-1}$. The 95^{th} percentile is shown in each grid cell. Calculations (Rapp et al., 2001) are based on the FAB model. The acid deposition has decreased considerably since the 80s but still there is some exceedance left in 2010 when the protocol is fully implemented. The number of lakes with exceedance for 1980, 1990, 1997 and 2010 corresponds to 51, 33, 17 and 11% of Swedish lakes.

Uncertainties are expected and become more important

The development of the critical load concept gathered speed in the late 80s and in the time that followed great efforts were made to develop models for mapping the sensitivity to sulphur and nitrogen compounds in Europe. Clearly, there are uncertainties in the models; they are always simplifications of reality. The availability of input data may be limited and thus default values based on estimates replace the missing data. Moreover, several assumptions are made to transform the biological reality into critical load numbers in order to make the concept feasible.

In the beginning of the 90s, the concept was, as a rule, not questioned since the acid deposition for large areas were way above the critical load. At that time the uncertainties were overshadowed by the deposition. Today the situation is quite different. For large areas in Europe the deposition is approaching the critical load, so now small changes in acid deposition and exceedances may be overshadowed by the uncertainties. Therefore, it has become important to take into account the uncertainties of the critical load concept when arguing for further emission reductions. This will increasingly be the case in the future. Thus problems will arise if critical load values are treated as hard numbers known with absolute accuracy (Skeffington, 1999). Therefore a more realistic view of the critical load concept would be to treat critical load numbers in a risk perspective (Barkman, 1997) instead of threshold values above which environmental damage occurs.

One of the aims of the Copenhagen Critical load Conference in 1999 (Løkke, *et al.,* 2000) was to "critically review methodologies for calculating critical loads for acidification and eutrophication''. The workshops dealt with criteria, methods, ecological indicators, validation and freshwaters. One of the overall conclusions of the conference was to recommend "continued scientific work and monitoring to improve methodologies and data for assessing the status of terrestrial ecosystems, soils, freshwaters and ground water, in particular in relation to their protection from acidifying and eutrophying pollutants". Moreover, several future recommendations dealt with the need to take into account the uncertainties at different scales in deriving and mapping critical loads. Another important outcome of the conference was that more work is needed on dynamic modelling for mapping recovery of ecosystems.

These developments lend strong support to a growing awareness of the need for scrutinising different components of the critical load concept. This is also manifested by the report of the seventeenth session of the CLRTAP's Executive Body (UNECE, 1999) where it is stated that one future priority is "review and extension of existing protocols".

Objectives and Methods

The main objectives of this thesis are to test and elucidate critical load models for surface waters as well as to explore potential alternatives. Since sulphur and only the acidifying effect of nitrogen are considered, this thesis considers the critical load of actual acidity, i.e. BC_w-$ANC_{le,crit}$ (Hettelingh *et al.*, 1991). As a result there is an emphasis on determination of the weathering rate.

Model output is often tested by comparison to measured data. Such a comparison is not feasible, however, because of the underlying steady-state assumption of CL models (i.e. we have no water chemistry data from either a pre-industrial steady state period or a future steady-state period). Nevertheless, even if we are not able to directly test CL models in this way, we can compare two models. Assuming lakes in the pre-industrial era were at steady-state, we can use palaeolimnological investigations (Korsman and Birks, 1996) for testing CL model estimates of this pre-industrial lake chemistry. While this is not a direct test against measured data, the palaeolimnology approach is probably more reliable than CL models. Palaeolimnology is used for testing CL models in Paper II and IV.

Exploring existing and alternative models refers to investigating critical components of the models, the implications of using the models and also the issue of whether there are better alternatives. A key component of the FAB model is the weathering rate which is estimated by the Steady-State Water Chemistry model, SSWC, (Henriksen *et al.*, 1992). That involves consideration of the F-factor which is used for quantifying the relation between soil- and surface water acidification. This F-factor is discussed in all papers, in particular Paper III where its dynamic aspect is investigated by using the dynamic SAFE model (Warfvinge and Sverdrup, 1992a). An alternative to SSWC for calculating pre-industrial lake chemistry is the PROFILE model (Warfvinge and Sverdrup, 1992b), which is explored in Paper IV.

In addition, a variant of the SSWC model used in the Swedish Environmental Quality Criteria, EQC, (SEPA, 2000) for surface waters is employed to assess the acidification status of Swedish lakes (Paper I). While this study is not directly related to testing and exploring CL models, the methods and the obstacles dealt with are highly relevant to the more general problem of assessing acidification.

Three models of pre-industrial lake chemistry

The critical load of acidity for surface waters is closely connected to the condition before human impact (i.e. the pre-industrial state) as this gives information about the weathering rate. In this thesis there are three different approaches for estimating the pre-industrial chemistry; palaeolimnology, SSWC and PROFILE (Figure 7).

Palaeolimnological investigations in lake sediments (Paper II and IV)

Palaeolimnological research offers one way of estimating the pre-industrial chemistry. In Sweden a number of studies have been conducted *e.g.* Renberg *et al.* (1993a), Renberg *et al.* (1993b), Korsman *et al.* (1994), Korsman and Birks (1996) and Korsman (1999). Generally, this approach relies on the fact that lake sediments represent a historical archive that mirrors the lake through time. Sediment, mainly derived from the catchment and the life in the lake itself, is continuously deposited on the lake bottom. This accumulation forms a historical archive of the lake and its catchment. Sediment cores are sampled and the diatom assemblages in the cores are correlated to present lake chemistry parameters such as pH, colour and alkalinity using a statistical model. The levels in the core are also dated. The result is that pre-industrial pH, colour and alkalinity can be predicted. Diatom assemblages are particularly good pH indicators and pH is predicted with an uncertainty of about ± 0.3-0.4 pH units or better in the studies used in this thesis. Despite the uncertainties, this approach is likely to represent the most reliable predictions there are, with reference to pre-industrial lake chemistry.

Steady State Water Chemistry (Paper I, II and III)

The Steady State Water Chemistry model, SSWC, has been widely used for calculating critical loads for surface waters in the Nordic countries (Henriksen *et al.,* 1990; Henriksen *et al.,* 1992; Henriksen *et al.,* 1993). The basic idea of the model is to estimate the non-marine (*) pre-industrial (o) concentration of base cations, $[BC^*]_o$, (including the weathering rate). The approach is to proceed from the present concentration of base cations, $[BC^*]_t$, in the lake and then predict how much $[BC^*]_t$ has changed due to acid deposition and forestry. This is accomplished by the means of the F-factor which estimates the quantity of base cations leaching out from the soils and/or are removed by harvesting. The F-factor is defined as the change in base cation concentration divided by the change in the sulphate concentration, at any time t, relative to the situation in the pre-industrial period (equation 6):

$$F = \frac{\left[BC^*\right]_t - \left[BC^*\right]_o}{\left[SO_4^*\right]_t - \left[SO_4^*\right]_o} \qquad (6)$$

If we define lake- and soil acidification according to equation 7 and 8, the F-factor can be expressed as equation 9, which indicates that the F-factor equals one when the lake is not acidifying. The F-factor decreases as soil processes are progressively less capable of neutralising incoming acidity, which results in water acidification.

$$\textit{Lake acidification} = ANC_o - ANC_t \qquad (7)$$

$$Soil\ acidification \propto \left[BC^*\right]_t - \left[BC^*\right]_o \quad (8)$$

$$F = \frac{soil\ acidification}{water\ acidification\ +\ soil\ acidification} \quad (9)$$

In order to solve for $[BC^*]_o$, estimates of F and $[SO_4^*]_o$, are needed. Empirical equations for estimating F can be found in the literature (Paper III) which rely on measuring some aspect of contemporary water chemistry. The equation for estimating $[SO_4^*]_o$, rests on the assumption that $[SO_4^*]_o$, is composed of two parts, one from background deposition and another one from weathering, which is linearly dependent on the concentration of base cations in the lake, e.g. as proposed by Wilander (1994):

$$\left[SO_4^*\right]_o = 5 + 0.05 \cdot \left[BC^*\right]_t \quad \mu eq\ L^{-1} \quad (10)$$

The PROFILE model (Paper IV)

The PROFILE model (Warfvinge and Sverdrup, 1992b; Sverdrup and Warfvinge, 1992) is a biogeochemical process-oriented model that calculates soil chemistry, including the weathering rate, in a soil profile. This model has been used for soil critical loads in Sweden and Denmark (Posch *et al.,* 1997) and was once used to predict surface water critical loads (Downing *et al.,* 1993).

The PROFILE model bases the weathering estimate on the properties of the soil, together with related climatic and hydrological factors. Natural soil horizons are simulated by a series of continuously stirred tank reactors in which the soil processes occur. In principle, the model procedure starts with the inflow of precipitation to the first layer, thus yielding a starting ANC. On the way down through the soil layers, ANC may either increase (weathering, uptake of nitrate) or decrease (uptake of base cations and ammonium as well as nitrification). A corresponding pH can be calculated by quantifying the CO_2 -, aluminium and organic acid buffering systems. The ANC of the water leaving the soil is assumed to correspond to lake chemistry. The pre-industrial chemistry is achieved by estimating the pre-industrial precipitation chemistry that is an input data to the model.

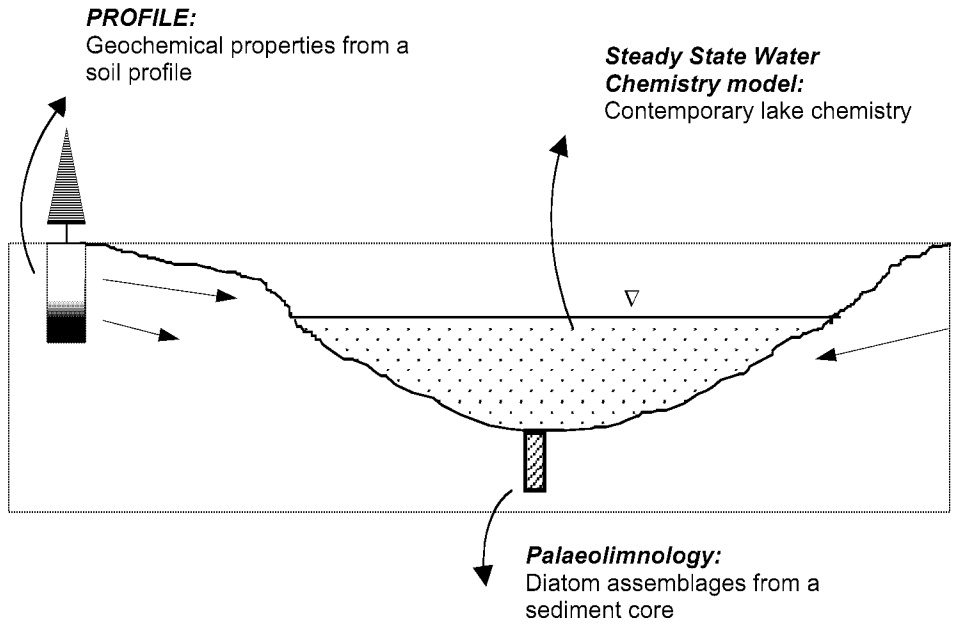

Fig. 7. A conceptual view of three models for calculating pre-industrial lake chemistry. Diatom reconstructions utilise the correlation between lake water pH and diatom assemblages in the sediment. SSWC proceeds from contemporary lake chemistry and uses empirical relationships for estimating how lake chemistry has changed due to acid deposition relative to pre-industrial times. PROFILE estimates the runoff chemistry from a soil profile based on soil properties and precipitation chemistry representing the pre-industrial era.

Results and Discussion

Summary of Paper I

How many of Sweden's lakes are acidified? Despite the intense research on acidification the last 30 years, this question is still of great concern, especially after the recent decline in acid deposition. To answer this question, the distinction between acid lakes and acidified lakes has to be clarified.

Acidification is a dynamic phenomenon (Odén, 1976), a process by which the environment is made more acidic. Therefore, it is necessary to study a lake through time to be able to evaluate if the lake is acidified. That is done by comparing the contemporary lake chemistry to the pre-industrial lake chemistry. The lakes which have acidified are identified as those for which the acidity has increased significantly. The lakes for which the acidity has not increased significantly are not acidified but some lakes may still be acid, which are referred to as the naturally acid lakes. These lakes can be defined as lakes with pre-industrial pH less than 6.

In this paper we use data from the 1995 Swedish Lake Survey (Wilander *et al.*, 1998) for documenting the current acidification status of Swedish lakes. The calculations are based on Sweden's new Environmental Quality Criteria, EQC (Wilander, 1998; SEPA, 2000) This is a comprehensive system for assessing the state of the aquatic environment and the degree to which human influence has altered that state, all on an integer scale from 1 to 5. The assessment of human influence on acidification is based on a variant of the SSWC model. The 4113 lakes from the Lake Survey (all greater than 4 ha in area), including some 800 affected by liming, were used in the calculations and scaled to all lakes in Sweden larger than 4 ha. An extension of the EQC methodology to estimate pH changes was also applied in which the partial pressure of CO_2 was considered.

A major choice in this assessment was whether to use ANC or alkalinity as the measure of buffering capacity. Depending on this choice, the proportion of Swedish lakes in the three most acidified classes varied between 5.5% and 8.5%. The number of moderately acidified lakes varied between 13% and 17%, and the population of insignificantly acidified lakes varied between 75% and 82%. In all cases, the alkalinity based assessment indicated a greater degree of acidification, as well as a greater regional extension of acidification outside of south-western Sweden. The proportion of naturally acid lakes with a pre-industrial pH below six was 8%. According to the EQC, naturally acid lakes were more likely to be acidified than the population of lakes as a whole.

Besides the choice between ANC and alkalinity, several other uncertainties are discussed. One is how to assess limed lakes in the calculations. The SSWC model cannot be applied directly to these lakes, so in our initial assessment, it was assumed that all limed lakes were indeed acidified. The sensitivity to this

assumption was illustrated by assuming that 30% of the limed lakes were in fact naturally acid. This reduces the population of Sweden's acidified lakes from 25% to 21% if alkalinity is used, and from 18% to 15% if ANC is used. The proportion of naturally acid lakes would also increase from 8 to 12%.

Another important source of uncertainty is the accuracy of the F-factor used in the SSWC model. If the F-factor is changed by ± 20%, the population of acidified lakes varies between 22% and 30% (when using the alkalinity method) and from 16% to 21% when using the ANC method.

The carbon dioxide pressure,P_{CO2}, influences the number of naturally acid lakes. If P_{CO2} is changed by ± 25%, the proportion of acidified lakes varies between 6.6 and 8.5%.

Summary of Paper II

Criteria are needed for distinguishing naturally acid water from that acidified by air pollution, especially in the organic-rich waters of northern Sweden. One way of supplementing the criteria for liming lakes in order to better identify naturally acid lakes would be to use the SSWC model to identify acid lakes that have not been acidified.

In this paper we test the SSWC model's predictions of pre-industrial chemistry with reference to palaeolimnology. In order to compare SSWC to the palaeolimnological reconstructions, with reference to pre-industrial pH and ANC, there were two obstacles that needed attention:

-The SSWC method does not include any pH prediction.

-The diatom reconstructions do not consider ANC, but alkalinity titrated to pH 5.4.

Adding a pH model involving the carbon dioxide and organic acid buffering systems overcame the first obstacle. The second obstacle was circumvented by using the Charge Balance Alkalinity (CBalk) approach suggested by Hemond (1990) which has proved to work well for Swedish surface waters (Köhler *et al.*, 2000). In the CBalk approach, ANC can be estimated from an endpoint titration and DOC. It can also be estimated with higher precision than from a charge balance between base cations and anions of strong acids. A reliable estimation of ANC can be crucial when modelling pH between 5 and 6.5 which is the pH range where many surface waters are weakly buffered. By using the CBalk approach, it was possible to convert diatom inferred pre-industrial alkalinity to ANC.

The SSWC method augmented by a pH model was compared to the palaeolimnological reconstructions (n=58) of pre-industrial pHo and ANCo, hereafter referred to as the Diatom model. The SSWC method was able to predict

pHo reasonably well in the higher pH range (>6.5). In the lower pH range, however, there were substantial deviations. In this pH region (n=24) only 8 lakes were within the uncertainty of the Diatom model and pHo was generally overestimated. These overestimates of pre-industrial pH's indicate that the use of the SSWC method for distinguishing acidified lakes from those which are not acidified would result in the liming of naturally acid lakes. The conversion from alkalinity and colour/DOC to pH could be one potential explanation for these discrepancies. However, testing the pH model using contemporary data did not reveal inaccuracies in the ANC/pH conversion that were similar in magnitude to the discrepancy between the SSWC method and the Diatom model.

A more likely explanation of the pHo discrepancy is the prediction of ANCo which the SSWC method overestimated for 33 lakes. This overestimate of ANCo originates from a difference in contemporary lake chemistry used in the SSWC method and the Diatom model. The lakes sampled for full chemistry in 1994 (input to SSWC) had, on average, 40% higher alkalinity than the lakes sampled in the late 80s, which were used for the calibration of the Diatom model. As in the case for critical load calculations, the sensitivity of SSWC to changes in contemporary lake chemistry complicate its use for predicting the steady-state situation in the pre-industrial period.

The large discrepancy between the SSWC predictions of pre-industrial lake acidity, and that inferred from the diatom data suggests that the SSWC model is not sufficiently accurate for use in planning the liming of individual lakes. Important as such results are for the Swedish liming program in northern Sweden, they are also of broader significance for acidification research in Europe. Steady-state water chemistry models are used to calculate the surface water critical loads for acid deposition. These critical loads are an important part of the scientific basis for the international protocols for reducing sulphur and nitrogen emissions to the atmosphere in Europe (Løkke, *et al.,* 2000). Palaeolimnological data on surface water chemistry could be used, as demonstrated in this paper, to test the steady-state water chemistry models upon which critical load values are based.

Summary of Paper III

The F-factor is a key component of the SSWC method. The F-factor estimates the degree to which acid deposition is neutralised before it reaches a lake at any particular point in time relative to the pre-industrial, steady-state water chemistry condition. This implies that the F-factor is a variable that changes in time during acidification and recovery. This dynamics of the F-factor as catchments acidify, and then recover are not widely recognised.

In this paper we will examine how well the empirical F-functions are able to estimate pre-industrial lake chemistry as lake chemistry changes during different phases of acidification and recovery. To accomplish this, we use the dynamic, process-oriented biogeochemical model SAFE to generate a plausible time series

of annual runoff chemistry for ca 140 Swedish catchments between 1800 and 2100. These annual hydrochemistry data are then used to generate empirical F-factors that are compared to the "actual" F-factor seen in the SAFE data for each "lake" and year in the time series.

Our results suggest that while the F-factor worked best within the acidification phase when it was introduced, the empirical F functions used for estimating F will be significantly in error during the recovery phase, when acid deposition has gone down significantly. The reason is that the F-factor should turn negative when the concentrations of base cations decrease below the pre-industrial level during the recovery phase, provided that the predictions of the SAFE model are reasonable.

Another important issue we want to emphasise is the way in which models such as SSWC will give different estimates of pre-industrial conditions (and therefore critical loads) depending on when a lake is sampled in the course of its acidification/recovery. This is a fundamental drawback that is not consistent with the concept of critical loads where the aim is to capture the long-term steady-state chemistry in the pre-industrial period, as a basis for calculating the ability of a site to tolerate a specific level of sustained acid deposition.

While the SAFE model does not provide us with the real truth, it offers a way to illustrate the interactions between water acidification and soil acidification i.e. the F-factor. If the water chemistry dynamics predicted by SAFE are a reasonable estimate of lake chemistry dynamics, then the empirical F-factor clearly inserts an appreciable amount of uncertainty into critical load calculations for surface waters. This will become more apparent in the years ahead now that acid deposition has declined considerably, and some recovery in runoff chemistry is widespread in Scandinavia.

Summary of Paper IV

A potential alternative to the SSWC method for determining surface water critical loads is the PROFILE model, a biogeochemical process-oriented model that calculates soil chemistry, including the weathering rate, in a soil profile. This model has been used for soil critical loads in Sweden and Denmark (Posch *et al.*, 1997) and was once used to predict surface water critical loads (Downing *et al.*, 1993).

The PROFILE model is based on an approach entirely different from that of the SSWC method. Instead of using contemporary lake chemistry to determine the pre-industrial weathering rate, PROFILE bases the weathering estimate on the properties of the soil, together with related climatic and hydrological factors. A similar approach where catchment topography, land use and riparian zone geology are used for calculating freshwater critical loads has proved promising (Kernan *et al.*, 1998; Smart *et al.*, 1999).

In this paper we explore the potential of using the PROFILE model as an alternative to the SSWC method for calculating critical loads of acidity. Diatom reconstructions for five lakes in northern Sweden are used for comparison. The hypothesis is that the uncertainty in prediction of pre-industrial leaching of base cations is reduced, as soil properties instead of lake chemistry are used as input data.

Application of PROFILE to surface waters involves challenges not present in the application of PROFILE to soil critical loads. For soil critical loads, the chemistry in the rooting zone (≈0-0.5m) on an individual plot or stand is of interest. When applying PROFILE to surface water critical loads, though, soil thickness and water flow paths must be considered. Furthermore, the model must integrate the variation of soil properties and hydrology across the entire lake catchment. The SSWC method avoids this integration problem by relying on lake chemistry that integrated the output of the entire catchment. So while the direct consideration of soil properties promises a more reliable and stable estimate of $[BC^*]_o$, there are problems of data acquisition, hydrology and spatial integration that need attention.

The PROFILE model requires a great deal of soil data for its implementation, which is not available on a catchment level. Therefore, we chose to use distributions of crucial parameters (soil depth, texture, moisture and mineralogy) from an area in the vicinity of five lakes for which diatom reconstructions were available. The PROFILE model was run using Monte Carlo sampling to generate a set of parameter values from the distributions. Using this approach, the PROFILE predictions of ANCo are a distribution of potential catchments that are compared to the local distribution of palaeolimnological reconstructions.

One of the most important concerns when modelling lake chemistry with PROFILE is to determine the hydrology of the catchment. That is not needed for the application to forest soils (nor is it readily determined from field data). When testing the PROFILE model by comparison to the diatom reconstructions, we used two hydrological extremes, as there are so many possibilities for how to route the water in a soil profile that lie between these two extremes. In one case, the whole soil profile was hydrologically active and thus contributing to weathering. The other case was where only 0.5 m of the soil was hydrologically active and contributing weathering products to runoff. The diatom predictions (median) were bracketed by the two hydrological extremes using the PROFILE model, but closer to the shallower routing. A calibration revealed that approximately 0.6 m of active soil was needed to get the PROFILE predictions to coincide with the diatom reconstructions, with reference to medians of ANC_o. This seems reasonable given what is known about the hydrology of the region. An important issue related to the effective depth is incorporation of lateral flow in the current model formulation. That will diminish the sensitivity in model output caused by variation in soil depth, but raises the question how to route the water

and how to adapt the weathering submodel to waters with residence times of months to decades.

Another concern is how to treat peatland in the calculations. The large part of the study area covered by peat (30%) was considered inert, and this is another source of uncertainty. We simply assumed that most runoff water runs through the upper peat layers where the fraction of mineral soil is negligible and the release of organic anions is accompanied by protons, which does not change ANC. However, if the counter ion is a cation such as sodium, ANC will certainly change. It is important to keep in mind the time perspective for such processes as short-term processes should not be taken into account in critical load calculations due to the underlying steady-state assumption. How to treat peatland is an important future concern, especially when applying the model in northern Sweden where a large part of the landscape is covered by peat.

At present, there is insufficient evidence to either recommend or reject the PROFILE model for surface water critical loads. The approach presented has to be tested for other regions and the uncertainties need further consideration.

Conclusions

It is more difficult to assess acidification than acidity, because the former requires knowledge of the past status as well as the present. Sweden's EQC for surface waters address this challenge with a methodology that can be applied to the extensive water quality records available in Sweden. Applying EQC to the data from the 1995 Swedish Lake Survey clearly documented the continued severity of surface water acidification in certain regions, as well as the extent of naturally acid lakes. Depending on the choice of buffering capacity i.e. alkalinity or ANC, the proportions of acidified lakes in Sweden were estimated to be 25 and 18%, respectively. Further consideration of that choice in a future revision of EQC would be of great value. The proportion of naturally acid lakes were estimated to 8%, but were influenced by the classification of limed lakes, the F-factor, and P_{CO2} in decreasing order of importance.

The SSWC method's prediction of pre-industrial pH did not correspond well with the diatom reconstructions for the lower pH range. Generally, pH was overestimated relative the diatom reconstructions due to substantially higher ANC levels. The discrepancies can be related to short-term fluctuations in modern lake chemistry. These results, together with the sensitivity of critical load estimates to changes in input data, illustrates the difficulties of using contemporary lake

chemistry data and empirical relationships to estimate the pristine steady-state situation, which is a central part of current critical load calculations for surface waters.

The dynamics of the F-factor as catchments acidify, and then recover are not widely recognised. Applying the F-factor approach to time series of runoff chemistry generated by the SAFE model suggests that the F-factor approach worked best during the acidification phase when soil processes buffer incoming acidity. However, the empirical functions for estimating F from contemporary lake chemistry are not well suited to the recovery phase when the F-factor turns negative due to recovery processes in the soil. Therefore, if SAFE's prediction of the F-factor bears a reasonable resemblance to lake chemistry dynamics, the empirical estimates of the F-factor are a significant source of uncertainty in the estimate of surface water critical loads and related calculations for quantifying lake acidification status.

Exploring the PROFILE model as an alternative to SSWC revealed that calculating critical loads for individual lakes is not feasible when using the PROFILE model due to lack of catchment specific input data. However, the use of distributions is possible since critical loads used in the international negotiations are not for individual sites but for populations of ecosystems in large areas. Furthermore, the statistical design of the Swedish National Survey of Forest Soils and Vegetation offers a way to compile a regional database to be used for calculating surface water critical loads. While direct considerations of soil properties instead of lake chemistry is promising, there are problems of hydrology, data acquisition and integration which will have to be overcome if PROFILE is to be a viable alternative for calculating surface water critical loads.

Future Challenges

The critical load of maximum sulphur, $CL_{max}(S)$, (equation 3) includes four components; BC^{*}_{dep} (non-marine fractions), BC_w, BC_u and $ANC_{le,crit}$. Using results from the latest Swedish CL calculations for surface waters (Rapp et al., 2001) offers a way to compare the magnitude of these components (Figure 8). If all data are included, $CL_{max}(S)$ is controlled by BC_w. Selecting lakes with low critical loads (below the 10^{th} percentile), however, results in a different pattern. In these lakes BC_w is still the most important, but the other components are nearly of the same magnitude.

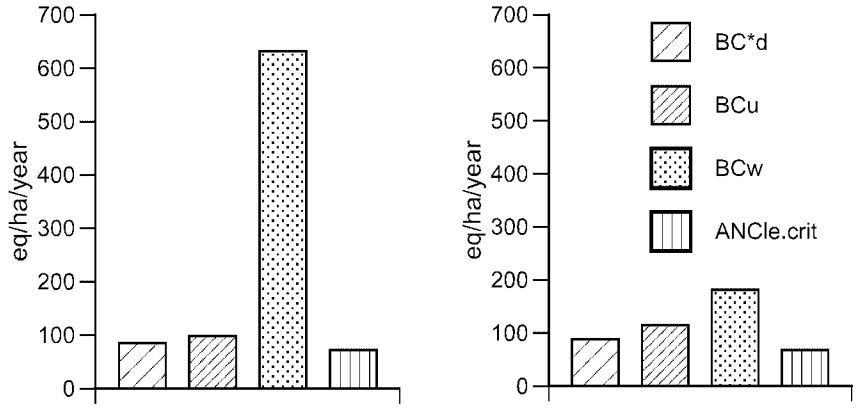

Fig. 8. The four components (medians) of $CL_{max}(S)$, using data from Rapp et al (2001). All data (left, n=2377) are used as well as the 10% lowest $CL_{max}(S)$, i.e. less than the 10th percentile (right, n= 238).

The calculation of $ANC_{le,crit}$, needs special attention. The critical chemical value, ANC_{limit}, is 20 μeq L^{-1} in the calculations (Figure 8) but it has been argued that this limit is far too low to protect sensitive fish species (Andersson, 2001). In fact, ANC_{limit} up to 150 μeq L^{-1}, has been proposed. Here it must be emphasised that such high levels might be relevant for protecting fish species, but they are not an appropriate representation of the conditions in the whole country during the pre-industrial era as predicted by the SSWC model. For the 2377 lakes from the 1995 Lake Survey to which SSWC was applied, about 1% of the lakes had ANC_o less than 20 μeq L^{-1}, 5% had an ANC_o less than 50 μeq L^{-1}, 15% had an ANC_o less than 100 μeq L^{-1} and 35% had an ANC_o less than 150 μeq L^{-1}. Thus defining a critical limit of 150 μeq L^{-1} would mean that in the pre-industrial period, over a third of Sweden's lakes would not have the ANC deemed needed for fish survival.

Another concern related to the choice of ANC_{limit} is the fact that the critical load turns negative to a greater degree if ANC_{limit} increases. If ANC_{limit} is set to 0, 20, 50 and 100 μeq/l, the proportion of lakes with negative critical load are 0.3, 2, 8 and 16% of all lakes, respectively. Increasing ANC_{limit} also has a large impact on the exceedances of the critical load (Figure 9).

In conclusion, this work highlights a number of new avenues for research. The weathering rate is generally seen as the key source of uncertainty in critical load calculations, but in areas where the critical loads are very low, other components such as deposition and uptake of base cations may also be just as crucial for the results. The choice of ANC_{limit} is also an important concern. The negative critical loads if one uses an ANC_{limit} allowing for good fish survival in contemporary Swedish lakes could indicate at least one of two things (and quite likely both). The first is that many Swedish lakes in the pre-industrial period had ANC values that were too low to ensure fish survival. The other possibility is that the other components in equation 3 are incorrect.

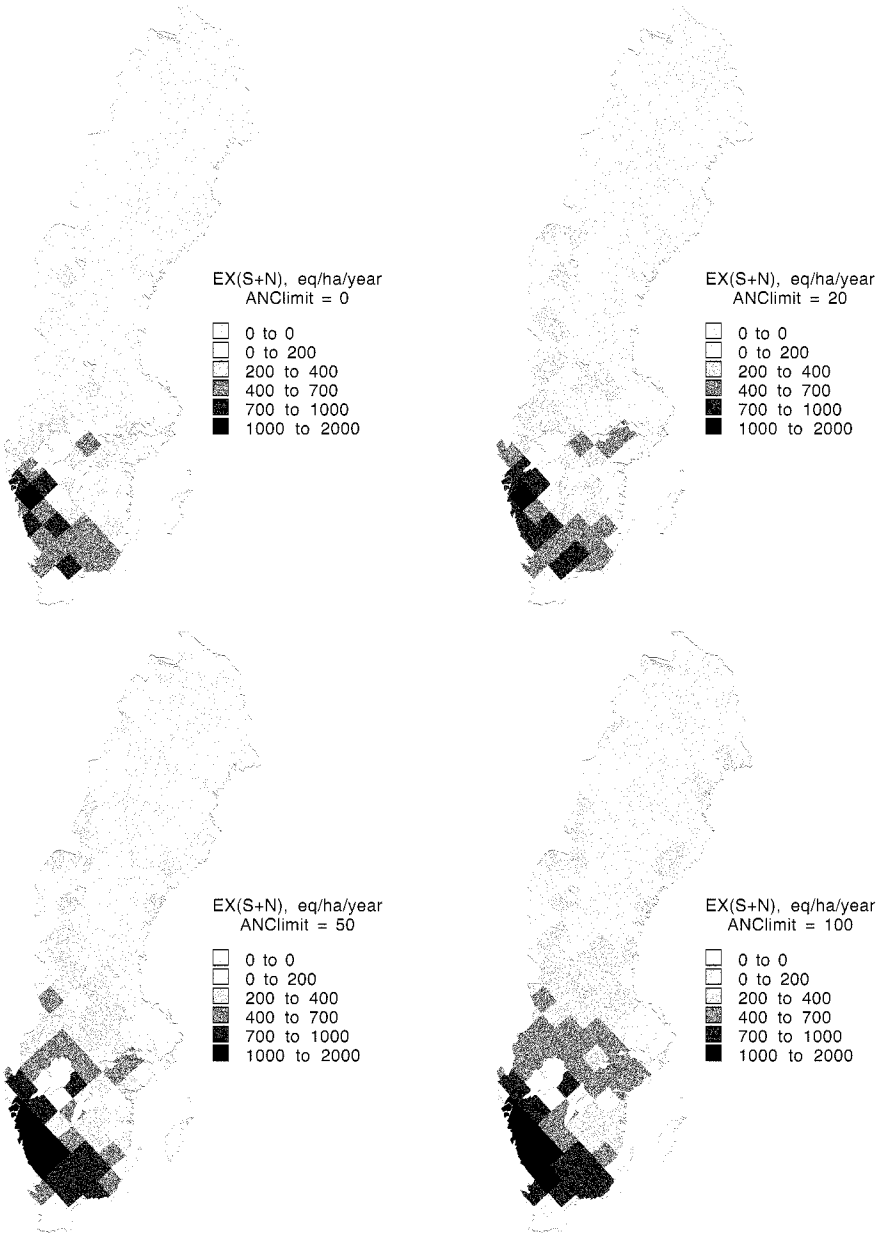

Fig. 9. Exceedance (eq ha^{-1} $year^{-1}$) in 1997 of critical loads (S+N) for surface waters in Sweden using different values of ANC_{limit}. The 95th percentile is shown in each grid cell. Calculations (Rapp *et al.*, 2001) are based on the FAB model. The number of lakes with exceedance using ANC_{limit} equal to 0, 20, 50 and 100 μeq L-1 corresponds to 15, 22, 32 and 47% of all lakes (n=2377).

References

Alcamo, J., Shaw, R. and Hordijk, L. (eds). 1990. The RAINS Model of Acidification: Science and Strategies in Europe. *Acad. Publ., Dordrecht*, the Netherlands.

Andersson, H.C. 2001. Är nuvarande kritiskt kemiska värden relevanta för att bedöma försurningspåverkan på fisk i svenska? *Department of Environmental Assessment, Report 2001: 5, Swedish University of Agricultural Sciences*, Uppsala.

Barkman, A. 1997. Applying the Critical Loads Concept: Constraints Induced by Data Uncertainty; Reports in Ecology and Environmental Engineering 1997:1*; University of Lund: Lund,* Sweden

Downing, R.J., Hettelingh, J.-P. and de Smet P.A.M. (eds.) (1993) Calculation and Mapping of Critical Loads in Europe-Status Report, Coordination Centre for Effects, *National Institute of Public Health and Environmental Protection (RIVM), Bilthoven*, The Netherlands. 163 pp. Report No. 259101003

Eldar, F.C. and Brydges, T. 1983. Effects of acid precipitation on aquatic regimes of Canada. Canadian Contribution to the Committee on the Challenges of Modern Society, NATO Panel 3, Report

Grennfelt, P. and Törnelöf, E. (eds) 1992. Critical Loads for Nitrogen-a workshop report, NORD 1992:41, *Nordic council of Ministers* ,Copenhagen.

Hemond, H.F. 1990. Acid neutralising capacity, alkalinity and acid-basew status of natural waters containing organic acids. *Environmental Science and Technology. 24(10)*, 1486-1489.

Henriksen, A., Forsius M., Kämäri J., Posch M. and Wilander A., 1993. Exceedance of critical loads for lakes in Finland, Norway and Sweden: Reduction requirements for Nitrogen and Sulphur deposition. Acid Rain Research Report 32/1993. *Norwegian Institute for Water Research (NIVA) Oslo,* Norway. 46 pp.

Henriksen, A., Kämäri, J., Posch, M. and Wilander, A., 1992. Critical Loads of Acidity: Nordic Surface Waters. *Ambio* 21(5), 356-363.

Henriksen, A., Lien, L. and Traaen, T.S. (1990) Critical loads for surface waters-chemical criteria for inputs of strong acids, Norwegian Institite for Water Research, Acid Rain Research Report 22/1990. *Norwegian Institute for Water Research,* Oslo, 45 p.

Hettelingh, J-P., Downing, R.J. and de Smet P.A.M. (eds) 1991. Mapping Critical Loads for Europé CCE Technical Report No.1, Coordination Centre for Effects, National *Institute of Public Health and Environmental Protection, Bilthoven,* The Netherlands, RIVM Report no. 259101001.

Hornung, M., Sutton, M. A. and Wilson, R. B. 1995. Mapping and Modelling of Critical Loads of Nitrogen: a Workshop Report. Proceedings of the Grange-Over-Sands Workshop, *Institute of Terrestrial Ecology, United Kingdom*: 207.

Kernan, M.R., Allot, T.E.H. and Batterbee, R.W. 1998. Predicting freshwater critical loads at the catchment scale: An empirical model, *Water, Air and Soil Pollution 105*: 31-41.

Korsman, T. 1999. Temporal and spatial trends of lake acidity in northern Sweden. *Journal of Paleolimnology 22*, 1-15

Korsman, T. and Birks, H.J.B. 1996. Diatom-based water chemistry reconstructions: a comparison of reconstruction techniques. *Journal of Paleolimnology, 15*, 65-77

Korsman, T., Renberg, I. and Anderson, N.J. 1994. A palaeolimnological test of the influence of Norway spruce (Picea abies) immigration on lake-water acidity. *The Holocene 4*, pp. 132-140

Kämäri, J., Jeffries, D. S., Hessen, D.O., Henriksen, A., Posch, M. and Forsius, M. 1992. Nitrogen critical loads and their exceedance for surface waters. In Critical loads for nitrogen, Nord 1992:41, (P. Grennfelt and E. Thörnelöf (eds*)), Nordic Council of Ministers, Copenhagen,* Denmark, pp. 161-200.

Köhler, S., Laudon, H., Wilander, A. and Bishop, K., 2000. Estimating organic acids dissociation in natural surface water using total alkalinity and TOC. *Water Research 34(5)*, 1425-1434.

Lundgren, J.T. 1991. Försurningen på dagordningen, *Swedish EPA,* Report 3886.

Løkke, H., Bak, J., Bobbink, R., Bull, K., Curtis, C., Falkengren-Grerup, U., Forsius, M., Gundersen, P., Hornung, M., Skjelkvåle, B. L., Starr, M., Tybirk, T. 1999. Conference Report Critical Loads Copenhagen 1999. *National Environmental Research Institute, DMU Report 121, Silkeborg*, Denmark

Nilsson, J. and Grennfelt, P. 1988. Critical Loads for Sulphur and Nitrogen. Report from a workshop held at Skokloster, Sweden, Organized by the *Nordic Council of Ministers. NORD* 1988:15

Odén, S. 1967. Nederbördens försurning, (in Swedish). *Dagens Nyheter,* 24 October, 1967

Odén, S., 1976. The Acidity Problem - An Outline of Concepts. *Water, Air, and Soil Pollution 6*, 137-166.

Posch, M., de Smet, P.A.M., Hettelingh, J.P. and Downing, R.J. 1999. Calculation and Mapping of Critical Thresholds in Europe, Status Report 1999. Bilthoven, The Netherlands, Coordination Center for Effects, *National Institute of Public Health and the Environment (RIVM).*

Posch, M., De Smet, P.A.M., Hettelingh, J-P. and Downing, Robert R.T. 1995. Calculation and Mapping of Critical Thresholds in Europe: Status Report 1995, CCE . *RIVM Report No. 259101004*, Bilthoven, the Netherlands.

Posch, M., Kämäri, J., Forsius, M., Henriksen, A. and Wilander, A. 1997. Exceedance for Lakes in Finland, Norway and Sweden: Reduction requirements for acidifying nitrogen and sulfur deposition. *Environmental Management 21(2),* 291-304.

Rapp, L., Wilander, A. and Bertills, U. 2001. Kritisk belastning för försurning av ytvatten. In Kritisk belastning för svavel och kväve, *Swedish Environmental Protection Agency*. In preparation

Renberg, I., Korsman, T. and Anderson, N. J., 1993. A Temporal Perspective of Lake Acidification in Sweden. *Ambio* 22(5), 264-271.

Renberg, I., Korsman, T. and Birks, H.J.B. 1993. Prehistoric increases in the pH of acid-sensitive Swedish lakes caused by land-use changes, *Nature Vol 362* 29 April 1993.

SEPA. 2000. Acidity/acidification, In: Environmental Quality Criteria - Lakes and Watercourses. *Swedish EPA Report 5050.*

Skeffington, R.A. 1999. The Use of Critical Loads in Environmental Policy Making: A Critical Appraisal, *Environmental Science & Technology*, June 1, 245-252.

Smart, R., Cresser, M.S., Billet, M.F., Soulsby, C., Neal, C., Wade, A., Langan, S. and Edwards, A.C. 1999. Modelling water chemical quality parameters for a major Scottish river, *Journal of Applied Ecology* (under review).

Sverdrup, H. and Warfvinge, P. 1992. Calculating field weathering rates using a mechanistic geochemical model PROFILE. *Applied Geochemistry 8*, 273-283.

Sverdrup, H., Henriksen, A. and De Vries, W. 1990. Mapping Critical Loads, A guidance to the criteria, calculations, data collection and mapping of critical loads. *Nordic Council of Ministers,* Copenhagen.

UBA, 1996. Manual on methodologies and criteria for mapping critical levels/loads and geographical areas where they are exceeded. UN/ECE Conventionon Long-range Transboundary Air Pollution. *Federal Environmental Agency (Umweltbundesamt)*, Texte 71/96, Berlin.

UNECE 1994. Protocol to the 1979 Convention on Long-range Transboundary Air Pollution on Further Reduction of Sulphur Emissions. *United Nations Economic Commission for Europe.*

UNECE 1999. Report of the seventeenth session of the executive body, Annex III, Decision 1999/2 concerning the structure and organization of work, *www.unece.org*

UNECE 1999. The 1999 Gothenburg Protocol to Abate Acidification, Eutrophication and Ground-level Ozone, *www.unece.org*

Warfvinge, P. and Sverdrup, H. 1992a. Hydrochemical modeling, In P. Sandén and P. Warfvinge (eds) Modelling Groundwater Response to Acidification. Norrköping, *Swedish Meteorological and Hydrological Institute (SMHI)*: 79-114.

Warfvinge, P. and Sverdrup, H. 1992b. Calculating Critical Loads of Acid Deposition with Profile-A Steady State Soil Chemistry Model. *Water, Air and Soil Pollution 63*, 119-143.

Wilander, A. 1994. Estimation of Background Sulphate Conentrations in Natural Surface Waters. *Water, Air and Soil Pollution 75*, 371-378.

Wilander, A. 1998. Surhet/försurning, In: Widerholm, T. (Ed.). Bedömningsgrunder för miljökvalitet-Sjöar och vatttendraf. Bakgrundsrapport 1-Kemiska och fysikaliska parametrar. *Swedish EPA* Report 4920. (In Swedish with English summary): 206.

Wilander, A., Johnson, R., Goedkoop, W. och Lundin, L. 1998. Riksinventeringen 1995; En synoptisk undersökning av vattenkemi och bottenfauna i svenska sjöar och vattendrag. - Rapport 4813, *Swedish EPA* (in Swedish with English summary)

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Åter till mannen med skägg. Han skulle bli biträdande handledare för mitt exjobb och han visade sig ha ett sju meter långt CV; vad säger man till en sådan? Det visade sig att han var kommunicerbar, mycket därtill, en trevlig prick faktiskt. Tack Kevin för ditt otroliga engagemang och inspirationsförmåga som gjort dessa år så spännande och lärorika. Mycket har vi gått igenom men vi fixade det till slut, Yes! (Jag ska försöka att undvika "based on pure guess work" i mina artiklar i fortsättningen)

Efter Lund bar det av till Umeå. Där fick jag lära mig att det inte finns propellrar i marken (det sa de ju i Lund). Det visade sig vara maskar (trist) som ser till att allting är homogent och fullständigt omblandat. Jag fick också lära mig att samsas med jägmästare, biologer, geografer, geologer, markkemister och norrlänningar, något som har varit till stor nytta. Jag vill tacka prefekt och tillika biträdande handledare Harald Grip (kommer du ihåg det?) för mina år på Skogsekologi. Alla ni som gjorde åren i Umeå så roliga ska ha ett stort jättetack; ni vet vilka ni är och det gör jag också!

Efter några år i norrland blev det flytt söderut (väldigt vad nära Dalarna jag har hamnat, nästan hemma!). Det var inte svårt att komma till rätta på Miljöanalys, en trevlig avdelning med en trygg och stabil ledningsgrupp. Ett speciellt tack vill jag rikta till Anders Wilander. Tack Anders för att du försöker hålla ordning på mig och berättar vad som verkligen händer i sjöarna. Mikael Östlund vill jag tacka för epspspdf-hjälp (även om han inte vet hur man laddar ett batteri). Liksom i Umeå har jag lärt känna många människor som jag sätter stort värde på (jag vet vilka ni är och det gör ni också).

Förutom mitt doktorerande har jag fått chansen att medverka i andra projekt, t.ex. "Mission Impossible". Jag vill tacka mina tappra kollegor Håkan Staaf och Ulla Bertills på Naturvårdsverket för ett trevligt och bra samarbete. Rapporten ska bli klar!

Till sist vill jag tacka mina föräldrar och mina syskon med familjer som alltid stöttar mig när det går åt skogen. Tänk vad bra jag har det!

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